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(54) Title: LIGHT AND THERMALLY STABLE POLYAMIDE (57) Abstract A light and thermally stable polyamide having built-in stabilizers is prepared by polymerizing polyamide-forming monomers in the presence of an effective amount of at least one hindered piperidine compound and at least one aliphatic, dicarboxylic acid chain regulating compound.		

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LIGHT AND THERMALLY STABLE POLYAMIDE

Description

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This invention relates to a polyamide that achieves high light and heat stability. More particularly, this invention relates to a modified nylon polymer containing a hindered piperidine compound and a chain regulator, wherein the modified nylon polymer has an improved stability to light and heat.

It is known that when unaided nylon is exposed to light and/or heat, the nylon discolours and loses its physical properties such as strength retention and resistance to elongation. Therefore, the addition of light and/or heat stabilizers to nylon is necessary in some cases in order for nylon to achieve acceptable performance. The stabilizers may be added before, during, or after polymerization. The conventional stabilizers are admixed with the polymer and are not bound to the polymer chain; therefore, during processing or use of the polyamide, the stabilizers can readily migrate out of the polymer, evaporate, or be washed out. This means that the activity of the stabilization is reduced in an undesired manner, and impurities are released to the surroundings (e.g., air, dye bath, etc.).

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Various organic stabilizers are known for use with nylon and articles manufactured therefrom. One problem, however, is that organic stabilizers such as, for example, hindered phenols, are expensive and have limited effectiveness.

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Inorganic stabilizers are generally less expensive and more effective than organic stabilizers; however, inorganic stabilizers suffer from a different set of problems. Typically, common inorganic stabilizers such as, for example, copper compounds, cause problems during processing. For example, in the melt extrusion process, copper compounds, may be reduced to insoluble elemental copper. Formation of elemental copper reduces production efficiency and adds significant equipment maintenance costs. Furthermore, the removal of copper deposits generates environmentally-undesirable effluent. In other processes such as, for example, the treatment of automotive nylon fibers with copper complexes in a dye bath, the excess copper complexes that are in the bath also produce environmentally-undesirable effluent.

Commonly owned United States Serial No. 08/804,312 relates to a process for preparing photochemically-stable, dyed nylon compositions comprising providing to a dye bath a shaped article of

poly(epsilon-caprolactam) hydrolytically polymerized in the presence of water and a hindered piperidine derivative and, in the dye bath, dyeing the shaped article with one or more metalized or nonmetalized acid dyestuffs.

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Commonly owned United States Serial No. 60/045,269 relates to a process for making stabilized solution-dyed fibers by melting a polyamide comprising amide monomers polymerized in the presence of at least one hindered piperidine compound and coloring the

10 melted polyamide with a colorant.

A PCT application, International Application No. PCT/EP 95/01349, describes an inherently stabilized polyamide containing at least one triacetone diamine compound having a primary amino group

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(-NH₂) that reacts with a carboxy end group of the polyamide molecule during polymerization, thus rendering the polymer light and heat stable.

An essay in Poly. Deg. And Stab. 21, 251-262 (1988) describes the

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improvement of the light stability of polyamide 6/6 by the addition of 2,2,6,6-tetramethylpiperidin-4-ol ("TMP"). In a recondensation of the TMP-containing polyamide 6/6 in the melt at 275°C under an atmosphere of water vapor, the authors claim that TMP reacts with the carboxyl end groups of the polyamide.

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A need, therefore, exists for a modified polyamide that reduces the need for copper-based stabilizers and that avoids discoloration, i.e., yellowing, after exposure to light and/or heat. Furthermore, it would be desirable to produce a polyamide having an

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improved resistance to yellowing upon exposure to light and/or heat, especially in engineering plastics applications.

It is an object of the present invention to provide a modified polyamide that avoids discoloration after exposure to light and/

35

or heat.

Another object of the present invention is to reduce the need for copper-based stabilizers in polyamides.

Yet another object of the present invention is to provide an environmentally-friendly and efficient process of producing a modified polyamide that is both light and heat stable.

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Thus, according to one embodiment of the present invention, there

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is provided a method of making a light and thermally stable polyamide with built-in stabilizers. The method comprises subjecting one or more polyamide-forming monomers to a polymerization pro-

cess in the presence of an effective amount of at least one hindered piperidine compound and an effective amount at least one aliphatic, dicarboxylic acid chain regulating compound.

- 5 In another aspect, the present invention is directed to a light and thermally stable polyamide comprising a backbone polymer chain, at least one hindered piperidine radical, and at least one aliphatic, dicarboxylic acid chain regulating compound wherein the at least one hindered piperidine radical and the at least one
10 aliphatic, dicarboxylic acid chain regulating compound are chemically bonded to the backbone polymer chain. The polyamide of the present invention is substantially free from copper compounds.
- 15 The modified polyamide with built-in stabilizers made according to the present invention achieves good light and heat stability without the use of other stabilizers such as, for example, copper salts. The combination of at least one aliphatic, dicarboxylic acid chain regulating compound and at least one hindered
20 piperidine compound not only functions as a molecular weight regulator in the polymerization process, but also endows the resulting polyamide with light and heat stability. The modified polyamide of the present invention does not discolor in the early stage of ultraviolet exposure.
- 25 The above and other objects, effects, features, and advantages of the present invention will become more apparent from the following detailed description of the preferred embodiments thereof, particularly when viewed in conjunction with the accompanying fi-
30 gures.

FIG. 1 is a graph illustrating the percent strength retained for solution-dyed yarns after exposure in a weatherometer.

- 35 FIG. 2 is a graph illustrating the yellowing of polymer plaques after exposure in a weatherometer.

To promote an understanding of the principles of the present invention, descriptions of specific embodiments of the invention
40 follow, and specific language is used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is intended by the use of this specific language and that alterations, modifications, equivalents, and further applications of the principles of the invention discussed are con-
45 templated as would normally occur to one of ordinary skill in the art to which the invention pertains.

As used herein, the term "polyamide" denotes homopolymers, copolymers, blends, and grafts of those long chain polymers having recurring amide groups (-CO-NH-) as an integral part of the main polymer chain. These long chain polyamides are generally referred to as "nylons."

As used herein with respect to the polyamide of this invention, the term "built-in" means that the components that render the polyamide light and heat stable are chemically bonded to the backbone polymer chain of the polyamide rather than merely physically admixed with the polyamide.

In one embodiment, the present invention is a modified polyamide substantially free of copper compounds comprising a backbone polymer chain, at least one hindered piperidine radical, and at least one aliphatic, dicarboxylic acid chain regulating compound wherein the at least one hindered piperidine radical and the at least one aliphatic, dicarboxylic acid chain regulating compound are chemically bonded to the backbone polymer chain. The light and thermally stable polyamide of the present invention may be nylon 6, nylon 6/6, nylon 6/9, nylon 6/10, nylon 6T, nylon 6/12, nylon 4/6, nylon 11, nylon 12, or aromatic nylons such as, for example, poly(meta-phenylene isophthalamide) and poly(para-phenylene terephthalamide). Preferably, the light and thermally stable polyamide of this invention is nylon 6, nylon 6/6, nylon 6T, nylon 6/12, and nylon 4/6. Most preferably, the light and thermally stable polyamide of the present invention is nylon 6.

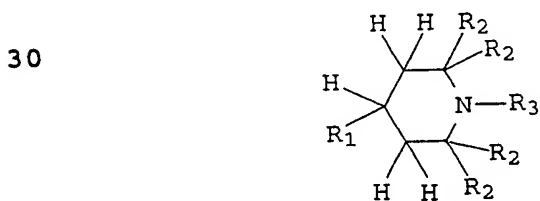
Any suitable polyamide-forming monomers may be used to form the light and thermally stable polyamide of the present invention. Nonlimiting examples of such suitable polyamide-forming monomers are diamine compounds, dicarboxylic acids, caprolactam monomers, and combinations thereof. In a preferred embodiment of the present invention, the polyamide-forming monomers are composed of caprolactam monomers.

The polymerization process by which the polyamide of the present invention is formed is preferably carried out according to conventional processes such as, for example, those described in U.S. Patent No. 5,149,758 to Matthies, the entirety of which is herein incorporated by reference, except that the polymerization of the present invention is carried out in the presence of an effective amount of one or more hindered piperidine compounds and an effective amount of one or more aliphatic, dicarboxylic acid chain regulating compounds. An effective amount of at least one hindered piperidine compound is an amount sufficient in combination with the one or more aliphatic, dicarboxylic acid chain regulating

compounds to render the resultant polyamide light and thermally stable. Preferably, the effective amount of the one or more hindered piperidine compounds is in the range of about 0.030 to about 0.800, and more preferably about 0.060 to about 0.400, mole percent based on the weight of the polyamide-forming monomers used. An effective amount of at least one aliphatic, dicarboxylic acid chain regulating compound is an amount sufficient in combination with the one or more hindered piperidine compounds to render the resultant polyamide light and thermally stable. Preferably, the effective amount of the one or more aliphatic, dicarboxylic chain regulating compounds is in the range of about 0.001 to about 0.800, and more preferably about 0.050 to about 0.500, mole percent based on the weight of the polyamide-forming monomers used.

To make the polyamide of the present invention, the one or more hindered amine compounds and the one or more aliphatic, dicarboxylic acid chain regulating compounds are added to the starting monomers or to the polymerizing reaction mixture. Thus, the one or more hindered piperidine compounds, the one or more aliphatic, dicarboxylic acid chain regulating compounds, and the polyamide-forming monomers may be added separately or as a mixture to a reactor in which polymerization is effected.

The hindered piperidine compound used in the present invention is represented by the formula:



35 wherein R_1 comprises an amine- or amide-forming functional group, R_2 is an alkyl, and R_3 is selected from the group consisting of hydrogen, C_1 - C_3 alkyl groups, and $-OR_4$ where R_4 is selected from the group consisting of hydrogen, methyl, and C_1 - C_7 alkyl groups.

40 R_1 is preferably selected from the group consisting of $-NHR_5$ where R_5 is hydrogen or a C_1 - C_8 alkyl, carboxyl, carboxylic acid derivative, $-(CH_2)_x(NH)R_5$ where x is an integer of from 1 to about 6, $-(CH_2)_yCOOH$ where y is an integer of from 1 to about 6, and $-(CH_2)_yCOOH$ acid derivative. The hindered piperidine compound used

45 in the present invention is preferably an amino polyalkylpiperi-

dine or a polyalkylpiperidine acid. Nonlimiting examples of such hindered piperidine compounds include:

- 4-amino-2,2,6,6-tetramethylpiperidine;
- 5 4-(aminoalkyl)-2,2,6,6-tetramethylpiperidine;
- 4-(aminoaryl)-2,2,6,6-tetramethylpiperidine;
- 4-(aminoaryl/alkyl)-2,2,6,6-tetramethylpiperidine;
- 3-amino-2,2,6,6-tetramethylpiperidine;
- 3-(aminoalkyl)-2,2,6,6-tetramethylpiperidine;
- 10 3-(aminoaryl)-2,2,6,6-tetramethylpiperidine;
- 3-(aminoaryl/alkyl)-2,2,6,6-tetramethylpiperidine;
- 2,2,6,6-tetramethyl-4-piperidinecarboxylic acid;
- 2,2,6,6-tetramethyl-4-piperidinealkylcarboxylic acid;
- 2,2,6,6-tetramethyl-4-piperidinearylcarboxylic acid;
- 15 2,2,6,6-tetramethyl-4-piperidinealkyl/arylcarboxylic acid;
- 2,2,6,6-tetramethyl-3-piperidinecarboxylic acid;
- 2,2,6,6-tetramethyl-3-piperidinealkylcarboxylic acid;
- 2,2,6,6-tetramethyl-3-piperidinearylcarboxylic acid; and
- 2,2,6,6-tetramethyl-3,4-piperidinealkyl/arylcarboxylic acid.

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The hindered amine compound may be a mixture of hindered piperidine compounds as well. More preferably, the hindered piperidine compound is a 2,2,6,6-tetraalkylpiperidine. Most preferably, the hindered piperidine compound is 4-amino-2,2,6,6-tetra-

25 tramethylpiperidine.

Suitable chain regulating compounds for use in the present invention are aliphatic, dicarboxylic acids and combinations thereof. Non-limiting examples of such aliphatic, dicarboxylic acids include the following:

- malic acid;
- malonic acid;
- methoxymalonic acid;
- 35 ethoxymalonic acid;
- butoxymalonic acid;
- dimethoxymalonic acid,
- succinic acid;
- methoxysuccinic acid;
- 40 2,2-dimethoxysuccinic acid;
- 2,3-dimethoxysuccinic acid;
- 2-ethyl-2-methoxysuccinic acid;
- glutaric acid;
- 2,2-dimethylglutaric acid;
- 45 2,3-dimethylglutaric acid;
- 2,4-dimethylglutaric acid;
- adipic acid;

- 3-methyladipic acid;
azelaic acid;
pimelic acid;
sebacic acid;
5 decanedicarboxylic acid; and
dodecanedioic acid.

The aliphatic, dicarboxylic acid chain regulating compound used in the present invention may be the same or different from a
10 dicarboxylic acid that is used as a polyamide-forming compound.
The aliphatic, dicarboxylic acid chain regulating compound is preferably selected from the group consisting of C₄-C₁₀ alkane dicarboxylic acids, particularly adipic acid, azelaic acid, sebacic acid, and decanedicarboxylic acid. Most preferably, the
15 aliphatic, dicarboxylic acid chain regulating compound is adipic acid.

Of course, various non-stabilizing additives may be used in the modified polyamide of the present invention. These include, for
20 example and without limitation, lubricants, nucleating agents, antioxidants, antistatic agents, etc.

The present invention produces a modified polyamide that is stabilized from degradation by light and heat and that does not discolor, i.e., yellow, upon exposure to light and/or heat. With
25 the present invention, it is not necessary to use other stabilizers such as, for example, copper compounds, as additives, although other stabilizers may be present, if desired. If such other stabilizers are present, they are present in significantly reduced amounts. The elimination of such stabilizing additives reduces equipment maintenance costs and eliminates harmful effluents produced in the removal of stabilizer deposits.
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The present invention also produces a modified polyamide having
35 increased spinning efficiency. Spinning efficiency is increased by at least about 0.5 percent. Such increase in spinning efficiency translates into hundreds of thousands of dollars in reduced annual manufacturing costs. While not wishing to be bound by any theory, it is currently believed that the increased spinning
40 efficiency results from that fact that the modified polyamide of the present invention has a narrower molecular weight distribution than acetic acid- and propionic acid-regulated polyamides. For polymers having a relative viscosity of 2.7, the molecular weight distribution of the modified polyamide of the present invention is about 1.65 to about 1.80, and the molecular weight
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distribution of acetic acid- and propionic acid-regulated polyamides is about 1.90 to about 2.00.

The present invention is further directed to articles produced from the light and thermally stable polyamide of the present invention and to methods of producing such articles. Non-limiting examples of such articles include fibers, yarns, carpets, engineering plastics such as automotive parts, and the like. Fibers may be formed by subjecting the light and thermally stable polyamides of the present invention to any conventional fiber-forming process such as, for example, that disclosed in U.S. Patents Nos. 4,983,448 to Karageorgiou and 5,487,860 to Kent et al., the entirety of both of which are incorporated herein by reference. Preferably, the fiber-forming process involves rapidly spinning the light and thermally stable polyamide at take-off speeds of at least about 4,000 m/min. Engineering plastics may be formed by subjecting the light and thermally stable polyamides of the present invention to any conventional plastic-forming process such as, for example, that disclosed in U.S. Patent No. 5,474,853 to Watanabe et al., the entirety of which is incorporated herein by reference.

Fibers formed from the light and thermally stable polyamides of the present invention may be dyed with conventional dyes used to dye nylons such as, for example, metalized and non-metalized acid dyes. Usual dyebath conditions for dyeing nylon can be employed. The following general conditions are exemplary and not intended to be limiting. A dyebath is prepared at a volume equal to about 20 times the weight of the articles to be dyed. Processing chemicals are added including a chelating agent to prevent the deposition or complexing of metal ions in hard water, a dye leveling agent, and, in the case of metalized acid dyes, an acid donor to slowly lower the dyebath pH. The dyestuff is added, and the dyebath pH is adjusted. The solution is heated to the desired temperature of typically about from 95°C to about 110°C at a rate of from about 0.5°C to about 3.0°C per minute and is held at that temperature for about 30 minutes to about 60 minutes. The dyebath is cooled or emptied, and the articles are thoroughly rinsed with fresh water. The dyed articles are dried in a tumble drier or an oven such as a Tenter oven.

Alternatively, fibers made from the light and thermally stable polyamides of the present invention may be solution-dyed before being formed into articles. Usual conditions for solution-dyeing nylon can be employed. The following general conditions are exemplary and not intended to be limiting. The polyamide of the present invention is melted and colored with a colorant selected

from the group consisting of pigments, dyes, any colored compound with properties between pigments and dyes, and combinations thereof. The colored polyamide is then spun into fibers or fabric according to conventional methods such as, for example, those disclosed in U.S. Patent No. 4,983,448 to Karageorgiou, U.S. Patent No. 5,487,860 to Kent et al., and U.S. Patent No. 4,918,947 to Speich. For engineering plastics, polymer chips are mixed with colored compounds such as, for example, pigments and dyes, before charging into an extruder. The mixing before being charged into the extruder is a physical mix, not a melt mix.

The invention will be further described by reference to the following detailed examples. The examples are set forth by way of illustration and are not intended to limit the scope of the invention. In the examples, "ADA" refers to adipic acid, "PPA" refers to propionic acid, "TPA" refers to terephthalic acid, and "TAD" refers to 4-amino-2,2,6,6-tetramethylpiperidine. Also as used in the examples, the following terms and test conditions are defined as follows:

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Weight Percent.

The weight percentage of that component in the charge.

25 Relative Viscosity (RV).

The relative viscosity compares the viscosity of a solution of polymer in formic acid with the viscosity of the formic acid itself (ASTM D 789). The test results reported herein were obtained using 0.20 g of nylon 6 dissolved in 20 cc. of formic acid at 25°C.

End Group Content.

35 The amino end group content is determined by dissolving about 2.0 g of the polymer in about 60 cc. of a phenol-methanol mixture (68:32). This solution is titrated with about 0.20 normal HCl at about 25°C by a potentiometric method, wherein the endpoint is determined by a steep potential increase.

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The carboxy end group content is determined by dissolving about 0.30 g of the polymer in about 40 cc. of a mixture of benzyl alcohol at 180°C. The solution is titrated with about 0.03 normal t-butyl ammonium hydroxide at about 80°C to about 100°C by a potentiometric method, wherein the endpoint is determined by a steep potential increase.

Exposure Test.

This test is designed to simulate extreme environmental conditions encountered inside a vehicle due to sunlight, heat, and humidity for the purpose of predicting the performance of automotive interior trim materials. This test measures the amount of yellowing (the delta b* value) of each of the exposed samples. This test is performed in accordance with the GM SAE J1885 Test Method, which is entitled "Accelerated Exposure of Automotive Interior Trim Components using a Controlled Irradiance Water-Cooled Xenon-Arc Apparatus."

Strength Retention.

This test is designed to determine the strength retention of the controls and the experimental samples. The term "strength retention" refers to the change in tenacity of the material as a result of exposure of the material to sunlight or an artificial light source. The tenacity is a measure of fiber strength. This test is performed in accordance with the AATCC Test Method 16-1993, *Colorfastness to Light, Option E (Water-Cooled Xenon-Arc Lamp, Continuous Light)*. The materials are exposed for 2125 kJ of exposure, and the tenacity of each material is measured before exposure and after each 425 kJ increment of exposure. Percent strength retention is determined as follows:

$$\frac{\text{Tenacity after exposure}}{\text{Tenacity before exposure}} \times 100\%$$

EXAMPLE 1 (Comparative)

Polymerization of PPA/TAD-Regulated Nylon 6

A mixture of 75 kg of caprolactam, 1800 g of water, 135 g (0.18 weight percent) propionic acid, and 112.5 g (0.15 weight percent) 4-amino-2,2,6,6-tetramethylpiperidine is charged into a 250-liter autoclave. The mixture is heated to 270°C in one hour, while the pressure increases to 60 psi (3102 mm Hg). After holding the mixture at 60 psi for 30 minutes, the pressure is slowly released. To accelerate the polymerization, the system is placed under a vacuum of 400 mm Hg for 75 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed with hot water (90°C) and dried in a tumble dryer. The relative viscosity measures 2.71. The amino group content measures 42 meq/kg, and the carboxylic end group content measures 45 meq/kg.

EXAMPLE 2

Polymerization of ADA/TAD-Regulated Nylon 6

5 A mixture of 75 kg of caprolactam, 1800 g of water, 240 g (0.32 weight percent) adipic acid, and 112.5 g (0.15 weight percent) 4-amino-2,2,6,6-tetramethylpiperidine is charged into a 250-liter autoclave. The mixture is heated to 270°C in one hour, while the pressure increases to 60 psi (3102 mm Hg). After holding the mixture at 60 psi for 30 minutes, the pressure is slowly released. To accelerate the polymerization, the system is placed under a vacuum of 500 mm Hg for 45 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed with hot water (90°C) and dried in a tumble dryer. The relative viscosity measures 2.67. The amino group content measures 37 meq/kg, and the carboxylic end group content measures 70 meq/kg.

EXAMPLE 3 (Comparative)

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Polymerization of PPA/0.15% TAD-Regulated Nylon 6

A mixture of molten caprolactam containing 0.5 by weight water and 0.19 by weight propionic acid is continuously introduced into the top of a polymerization reactor. The polymerization reactor used is a stainless steel VK column as outlined in U.S. Patent No. 4,354,020, which is incorporated herein by reference. The mixture is continuously introduced into the top of the VK column into reaction zone I at a temperature of about 265°C and at a rate of about 30-40 kg/h with stirring. The VK column, which has a capacity of 340 liters, is heated by heat exchange oil. At the same time, 4-amino-2,2,6,6-tetramethylpiperidine is continuously supplied from a separate stream to the reaction zone I at a rate so that there is 0.15 weight percent of 4-amino-2,2,6,6-tetramethylpiperidine in the mixture at all times. The heat of polymerization generated in further reaction zones is removed by appropriate cooling with internal heat exchangers. The temperature of the last reaction zone is about 265°C. The resulting polymer is extruded at the bottom of the VK column and cut into chips. The chips are washed with hot water (90°C) and dried in a tumble dryer. The relative viscosity measures 2.68. Both the amino group content and the carboxylic end group content measure 44 meq/kg.

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EXAMPLE 4

Polymerization of ADA/0.15% TAD-Regulated Nylon 6

- 5 Caprolactam is polymerized in the same VK column as in Example 3, but with the addition of 0.29 weight percent adipic acid, 0.5 weight percent water, and 0.15 weight percent 4-amino-2,2,6,6-tetramethylpiperidine. The dried product has a relative viscosity of 2.73, an amino end group content of 43 meq/kg, and a
- 10 carboxylic end group content of 59 meq/kg.

EXAMPLE 5

Polymerization of ADA/0.30% TAD-Regulated Nylon 6

- 15 Caprolactam is polymerized in the same VK column as in Example 3, but with the addition of 0.29 weight percent adipic acid, 0.5 weight percent water, and 0.30 weight percent 4-amino-2,2,6,6-tetramethylpiperidine. The dried product has a relative viscosity
- 20 of 2.70, an amino end group content of 53 meq/kg, and a carboxylic end group content of 51 meq/kg.

EXAMPLE 6 (Comparative)

- 25 Polymerization of TPA/0.15% TAD-Regulated Nylon 6

Caprolactam was polymerized in the same VK column as in Example 3 with addition of 0.30 weight percent terephthalic acid, 0.5 weight percent water, and 0.15 weight percent 4-amino-2,2,6,6-tetramethylpiperidine. The dried product had a relative viscosity

30 of 2.68, an amino end group content of 42 meq/kg, and a carboxylic end group content of 63 meq/kg.

EXAMPLE 7

- 35 Spinning of 1115 Denier/58 Filament Solution-Dyed Yarn with Tri-lobal Cross-Section

Nylon 6 polymer from Examples 3-6, as well as commercial nylon 6

40 (Ultramid B[®] nylon 6 available from BASF Corporation of Mount Olive, NJ), is extruded at 260°C-265°C. Opal gray color concentrate mixed with a proper amount of nylon chip is added to the spinning machine through volumetric feeders. The extruded filaments are cooled and solidified by a stream of quench air at 15°C.

45 After the application of spin finish, the yarns are drawn at a

draw ratio of 3.3 and are textured in a texture jet at 215°C. The yarns are taken up at a draw roll speed of about 2350 m/min.

EXAMPLE 8

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Strength Retention after Ultraviolet Exposure

Opal gray solution-dyed yarns from Example 7 are exposed in an Atlas Ci65 Weather-Ometer® for 2125 kJ exposure in increments of 425 kJ under the conditions specified by the AATCC Test Method 16-1993, *Colorfastness to Light*, Option E. The strength of each of the yarns is measured before exposure and after each 425 kJ increment of exposure. The percent strength retention after each increment of exposure is shown in FIG. 1. These results show a significant improvement in retained strength for the TAD-containing polymers, especially the ADA/TAD polymers. The commercial nylon 6 lost its strength dramatically during the exposure, while the TAD-containing polymers retained more than 85% of their strength after 2125 kJ of exposure.

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EXAMPLE 9

Yellowing of Plaques by GM SAE J1885 Test Method

Polymer from Examples 3-6, as well as commercial nylon 6 (Ultramid B® nylon 6 available from BASF Corporation of Mount Olive, NJ), is melted in an injection molding machine at about 265°C. The molten polymer is injected into a mold to make 110mm x 110mm x 3mm plaques. These plaques are then cut into smaller plaques, each measuring about 55mm x 110mm x 3mm.

The plaques are then exposed in an Atlas Ci65 Xenon-Arc Weather-Ometer® for 1,000 hours (1,410 kJ) in 100 hour (141 kJ) increments by the conditions specified in the GM SAE J1885 Test Method. The exposed plaques are measured for yellowing (or "Delta b*," where a higher Delta b* value indicates a more yellow sample) at each increment of exposure using an Applied Color Systems Spectrophotometer. The results of these exposures are plotted in FIG. 2. The results show that the commercial nylon 6 polymer and the comparative TPA/0.15% TAD-regulated polymer yellowed most significantly during the exposure. While exposure of the PPA/TAD polymer resulted in less yellowing than the commercial nylon 6 polymer and the comparative TPA/0.15% TAD-regulated polymer, exposure of the ADA/TAD polymers resulted only in minimal yellowing.

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While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalents arrangements included within the spirit and scope of the appended claims.

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Claims

1. A method for producing a light and thermally stable polyamide
5 comprising subjecting one or more polyamide-forming monomers to a polymerization process in the presence of an effective amount of at least one hindered piperidine compound and an effective amount of at least one chain regulating compound, wherein the at least one chain regulating compound comprises
10 an aliphatic, dicarboxylic acid and combinations thereof.
2. The method according to claim 1 wherein the at least one hindered piperidine compound is selected from the group consisting of amino polyalkylpiperidines.
- 15 3. The method according to claim 1 wherein the at least one hindered piperidine compound is selected from the group consisting of 4-amino-2,2,6,6-tetramethylpiperidine; 4-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 4-(aminoaryl)-2,2,6,6-tetramethylpiperidine; 4-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 3-amino-2,2,6,6-tetramethylpiperidine; 3-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 3-(aminoaryl)-2,2,6,6-tetramethylpiperidine; 3-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 2,2,6,6-tetramethyl-4-piperidinecarboxylic acid; 2,2,6,6-tetramethyl-4-piperidinealkylcarboxylic acid; 2,2,6,6-tetramethyl-4-piperidinearylc
20 arylcarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinecarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinealkylcarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinearylc
25 arylcarboxylic acid; 2,2,6,6-tetramethyl-3,4-piperidinealkyl/arylc
30 arylcarboxylic acid; and combinations thereof.
4. The method according to claim 3 wherein the at least one hindered piperidine compound is 4-amino-2,2,6,6-tetramethylpiperidine.
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5. The method according to claim 1 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is selected from the group consisting of malic acid; malonic acid; methylmalonic acid; ethylmalonic acid; butylmalonic acid; dimethylmalonic acid, succinic acid; methylsuccinic acid; 2,2-dimethylsuccinic acid; 2,3-dimethylsuccinic acid; 2-ethyl-2-methylsuccinic acid; glutaric acid; 2,2-dimethylglutaric acid; 2,3-dimethylglutaric acid; 2,4-dimethylglutaric acid; adipic acid; 3-methyladipic acid; azelaic acid; pi-
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melic acid; sebacic acid; decanedicarboxylic acid; dodecanedioic acid; and combinations thereof.

- 5 6. The method according to claim 5 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is selected from the group consisting of adipic acid, azelaic acid, decanedicarboxylic acid, sebacic acid, and combinations thereof.
- 10 7. The method according to claim 6 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is adipic acid.
- 15 8. The method according to claim 1 wherein the light and thermally stable polyamide is selected from the group consisting of nylon 6, nylon 6/6, nylon 6/9, nylon 6/10, nylon 6T, nylon 6/12, nylon 4/6, nylon 11, nylon 12, poly(meta-phenylene isophthalamide), and poly(para-phenylene terephthalamide).
- 20 9. The method according to claim 8 wherein the light and thermally stable polyamide is nylon 6.
- 25 10. The method according to claim 1 wherein the polyamide-forming monomers comprise caprolactam monomers.
- 30 11. A light and thermally stable polyamide comprising a backbone polymer chain, at least one hindered piperidine radical, and at least one aliphatic, dicarboxylic acid chain regulating compound, wherein both the at least one hindered piperidine radical and the at least one aliphatic, dicarboxylic acid chain regulating compound are chemically bonded to the backbone polymer chain.
- 35 12. The polyamide of claim 11 wherein the at least one hindered piperidine compound is selected from the group consisting of amino polyalkylpiperidines.
- 40 13. The polyamide of claim 11 wherein the at least one hindered piperidine compound is selected from the group consisting of 4-amino-2,2,6,6-tetramethylpiperidine; 4-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 4-(aminoaryl)-2,2,6,6-tetramethylpiperidine; 4-(aminoaryl/alkyl)-2,2,6,6-tetramethylpiperidine; 3-amino-2,2,6,6-tetramethylpiperidine; 3-(aminoalkyl)-2,2,6,6-tetramethylpiperidine; 3-(aminoaryl)-2,2,6,6-tetramethylpiperidine; 3-(aminoaryl/alkyl)-2,2,6,6-tetramethylpiperidine; 2,2,6,6-tetramethyl-4-piperidinecarboxylic acid; 2,2,6,6-tetramethyl-4-pi-

- peridinealkylcarboxylic acid; 2,2,6,6-tetramethyl-4-piperidinearylcarboxylic acid; 2,2,6,6-tetramethyl-4-piperidinealkyl/arylcarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinecarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinealkylcarboxylic acid; 2,2,6,6-tetramethyl-3-piperidinearylcarboxylic acid; 2,2,6,6-tetramethyl-3,4-piperidinealkyl/arylcarboxylic acid; and combinations thereof.
14. The polyamide of claim 13 wherein the at least one hindered piperidine compound is 4-amino-2,2,6,6-tetramethylpiperidine.
15. The polyamide of claim 11 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is selected from the group consisting of malic acid; malonic acid; methylmalonic acid; ethylmalonic acid; butylmalonic acid; dimethylmalonic acid, succinic acid; methylsuccinic acid; 2,2-dimethylsuccinic acid; 2,3-dimethylsuccinic acid; 2-ethyl-2-methylsuccinic acid; glutaric acid; 2,2-dimethylglutaric acid; 2,3-dimethylglutaric acid; 2,4-dimethylglutaric acid; adipic acid; 3-methyladipic acid; azelaic acid; pimelic acid; sebacic acid; decanedicarboxylic acid; dodecanedioic acid; and combinations thereof.
16. The method according to claim 15 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is selected from the group consisting of adipic acid, azelaic acid, decanedicarboxylic acid, sebacic acid, and combinations thereof.
17. The method according to claim 16 wherein the at least one aliphatic, dicarboxylic acid chain regulating compound is adipic acid.
18. The polyamide of claim 11 wherein the polyamide is selected from the group consisting of nylon 6, nylon 6/6, nylon 6/9, nylon 6/10, nylon 6T, nylon 6/12, nylon 4/6, nylon 11, nylon 12, poly(meta-phenylene isophthalamide), and poly(para-phenylene terephthalamide).
19. The polyamide of claim 18 wherein the polyamide is nylon 6.
20. A light and thermally stable polyamide comprising a backbone polymer chain, at least one hindered piperidine radical chemically bonded to the backbone polymer chain, and at least one aliphatic, dicarboxylic acid chain regulating compound chemically bonded to the backbone polymer chain, wherein the

spinning efficiency of the light and thermally stable poly-
amide is increased by at least 0.5 percent.

21. An article comprising the light and thermally stable poly-
amide of claim 11.
22. An article according to claim 21 wherein the article is se-
lected from the group consisting of fibers, yarns, carpets,
and engineering plastics.

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FIG.1

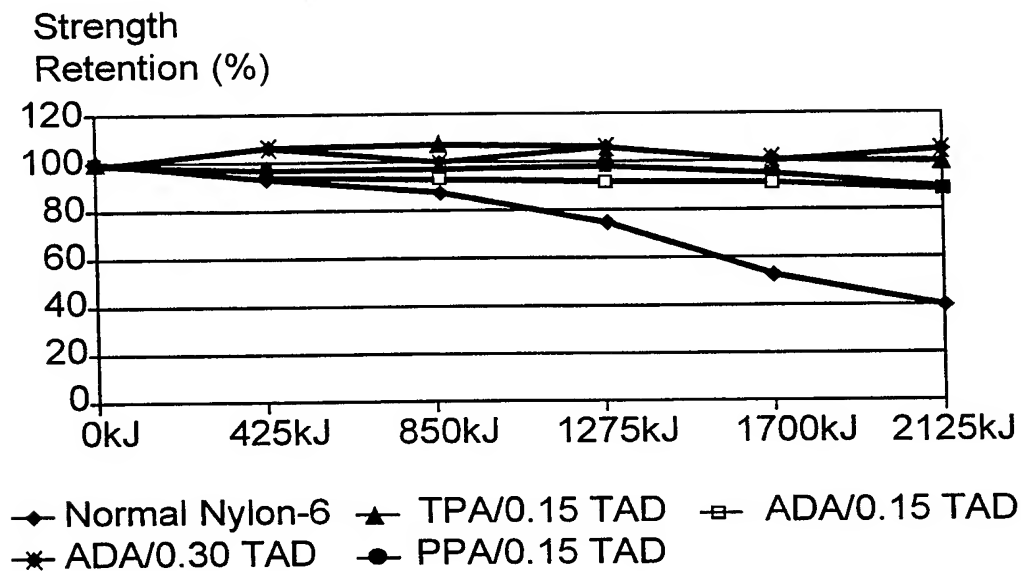
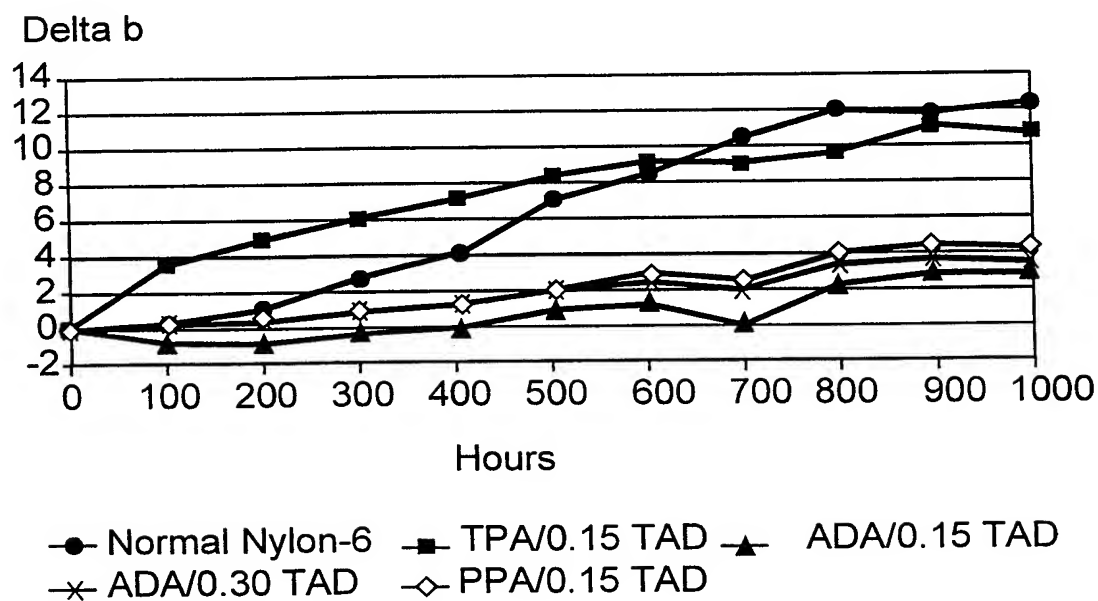


FIG.2



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/00889

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/3435 C08G69/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 822 275 A (BASF CORP.) 4 February 1998 see claims 1,4,7,11,14 ---	1-4, 11-14, 21,22
P,X	WO 98 50610 A (BASF CORP.) 12 November 1998 cited in the application see page 6, line 30 - line 33; claims 1-4,11,13,16-19 ---	1,11,21
A	WO 97 05189 A (ALLIED SIGNAL) 13 February 1997 see claims 1,11; example 1 -----	1,11,21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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